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## Pressure-cooking of explosives – the crystal structure of $\epsilon$ -RDX as determined by X-ray and neutron diffraction\*\*

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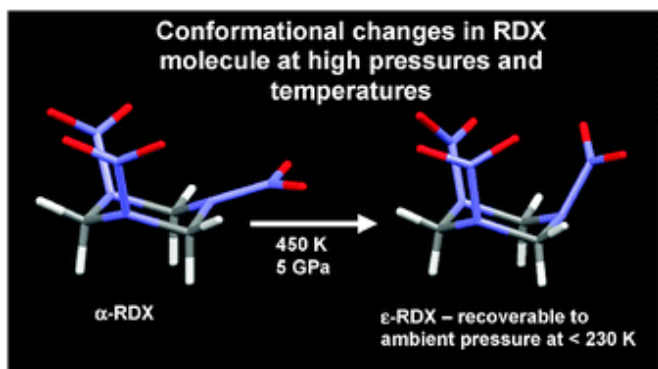
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### Supporting information:

Electronic supplementary information (ESI) available: Raman spectra recorded on decompression. CCDC 769778. For ESI and crystallographic data in CIF or other e-format see <http://dx.doi.org/10.1039/c0cc00368a>

### Graphical abstract:



## Abstract

The high-pressure, high-temperature  $\epsilon$ -form of the widely used explosive RDX has been structurally characterised using a combination of diffraction techniques, and a sample of this form has been successfully recovered to ambient pressure.

## Main text

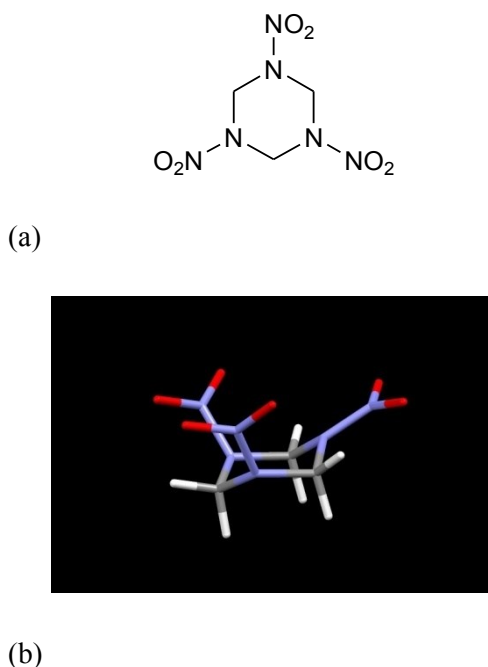
The performance of energetic materials (propellants and explosives) depends on several factors that include crystal density, detonation velocity, and sensitivity to detonation by stimulus.<sup>1</sup> These in turn are governed by the solid-state structure of the energetic material. In order to model and understand the characteristics and performance of these materials, it is essential to obtain detailed structural information over a range of conditions of temperature and pressure. This information can be used to explore aspects of energetic materials that include: sensitivity to shock, heat, and friction; chemical decomposition mechanisms; energy transfer through the solid; detonation velocities; and testing the efficacy of theoretical modelling techniques.

RDX (1,3,5-trinitrohexahydro-1,3,5-triazine) is a widely used military explosive that can be compounded with mineral jelly or polymers to form plastic explosives such as C4 and PBX compositions. Two polymorphic forms are known at ambient conditions, denoted as the  $\alpha$ - and  $\beta$ -forms, respectively. The structure of the orthorhombic  $\alpha$ -form has been determined by both single crystal X-ray<sup>2</sup> and neutron diffraction<sup>3</sup> and shows that the RDX molecule adopts a conformation in which two of the nitro-groups are in pseudo-axial positions and the other is in a pseudo-equatorial position – this is denoted as the AAE conformation (see Figure 1).  $\beta$ -RDX was first identified in 1950 by crystallisation from high boiling solvents such as nitrobenzene,<sup>4</sup> but on account of its high metastability it has eluded structural characterisation until recently.<sup>5</sup> In the crystal structure of the  $\beta$ -form both independent molecules adopt the chair conformation with all nitro groups in axial positions (AAA conformation), resulting in approximate  $C_{3v}$  molecular symmetry.<sup>5</sup>

Compression of the  $\alpha$ -form to pressures  $>3.9$  GPa at ambient temperature gives the  $\gamma$ -form, which has recently been structurally characterised by single crystal X-ray and neutron powder diffraction.<sup>6</sup> In this structure the two independent molecules in the asymmetric unit adopt conformations which are best described as AAA and AAI, respectively, where I represents an intermediate orientation of the  $\text{NO}_2$  group midway between axial and equatorial positions.

Recent spectroscopic studies have also suggested a further high-pressure form obtained above 17.8 GPa at ambient temperature, which has been denoted the  $\delta$ -form,<sup>7,8</sup> but this has not been structurally characterised. Two spectroscopic studies of RDX at elevated temperatures and pressures have suggested

the presence of yet another form of RDX. Baer *et al.* observed a transition to a new form at pressures >3.8 GPa and a temperature of 375 K using nitrogen as a pressure-transmitting medium.<sup>9</sup>

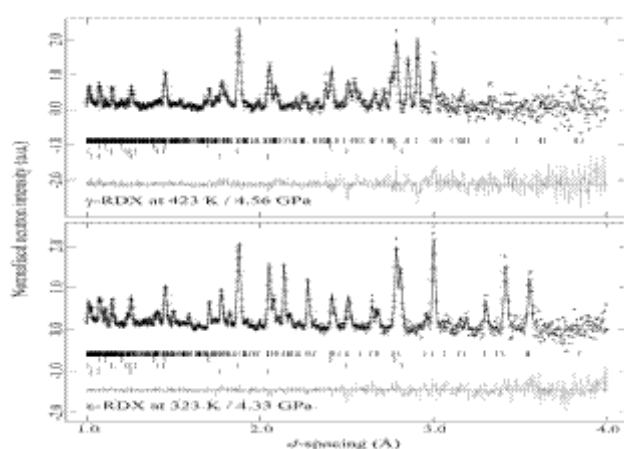


**Figure 1.** (a) Molecular structure of RDX; (b) The AAE conformation adopted by  $\alpha$ -RDX.

A later study by Miller *et al.* using Fluorinert as a pressure-transmitting medium also observed a transition at similar pressures, but at 488 K.<sup>10</sup> Due to similarities in vibrational spectra and the observation that this form persisted on decompression at ambient temperature almost to ambient pressure, both studies concluded that the high-temperature/high-pressure form of RDX is the  $\beta$ -form.

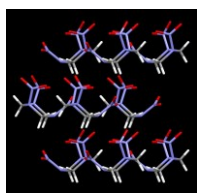
The main focus of the current study was to identify and characterise this high-pressure, high-temperature form and to investigate whether it could be recovered to ambient pressure. We therefore investigated this form by neutron powder diffraction, using a Paris-Edinburgh cell with a newly commissioned variable temperature insert.<sup>11</sup> A sample of  $\alpha$ -RDX- $d_6$  was first compressed to 4.3 GPa at 293 K (using MeOD/EtOD as a pressure-transmitting medium) to give  $\gamma$ -RDX, which was identified by its neutron powder diffraction pattern. After heating incrementally to 423 K, no changes were observed in the diffraction patterns, but on brief warming (30 minutes) to 448 K a new pattern was observed (see Figure 2). To avoid potential decomposition of the sample, the temperature was then reduced first to 323 K and then to 293 K; this new pattern persisted on cooling. Subsequent decompression at 293 K showed that this new form persisted to 0.99 GPa before transforming to the  $\alpha$ -form at 0.85 GPa. Comparison of these patterns with the pattern calculated from the crystal structure of the  $\beta$ -form allowed us to prove conclusively that the high-temperature/high-pressure form

of RDX is *not* the  $\beta$ -form obtained at ambient conditions, but instead represents a fifth polymorph, now denoted  $\varepsilon$ -RDX. Raman spectra of a non-deuterated sample of RDX contained in a diamond-anvil cell and subjected to a similar pressure and temperature regime were in excellent agreement with the spectra reported by Baer *et al.* and confirmed that on decompression the  $\varepsilon$ -form transformed directly to the  $\alpha$ -form without proceeding *via* the  $\gamma$ -form. Within experimental uncertainty the transition pressures obtained from the diffraction and Raman experiments were identical and agree with previous spectroscopic reports.<sup>9</sup> Based on these results the effects of deuteration on the  $\gamma \rightarrow \varepsilon$  and  $\varepsilon \rightarrow \alpha$  phase transitions appear to be negligible. This is also observed to be the case for the  $\alpha \rightarrow \gamma$  transition in RDX.<sup>6</sup>

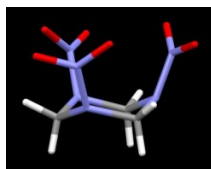


**Figure 2.** Neutron powder diffraction patterns for (a)  $\gamma$ -RDX- $d_6$  at 423 K/4.56 GPa and (b)  $\varepsilon$ -RDX at 323 K/4.33 GPa.

In order to obtain single crystal x-ray diffraction data for  $\varepsilon$ -RDX, a single crystal of  $\alpha$ -RDX contained in a diamond-anvil cell (DAC) was first pressurised to  $\sim 5.0$  GPa to give  $\gamma$ -RDX and then heated to 500 K. Unfortunately, the crystal dissolved in the hot pressure-transmitting medium MeOH/EtOH (4:1). This problem was overcome by loading a DAC with an excess of polycrystalline  $\alpha$ -RDX and pressurising to  $\sim 5.7$  GPa. On raising the temperature to 500 K for 1 h, the enhanced solubility combined with the reduced viscosity of the medium resulted in recrystallisation of the sample to give a single crystal large enough for single crystal X-ray diffraction. Structure solution and refinement showed that  $\varepsilon$ -RDX crystallises in the orthorhombic crystal system (space group  $Pca2_1$ ) with only one molecule in the asymmetric unit. With this structure as a starting point it proved possible to refine all of the neutron powder diffraction patterns extremely well (typical  $\chi^2$  values of 1.26) thus providing additional support that the structural model is correct. Figure 3a shows the packing of RDX molecules in the  $\varepsilon$ -form.



(a)



(b)

**Figure 3.** (a) Packing of RDX molecules in the  $\epsilon$ -form viewed along the b-axis, and (b) the AAA molecular conformation found in  $\epsilon$ -RDX.

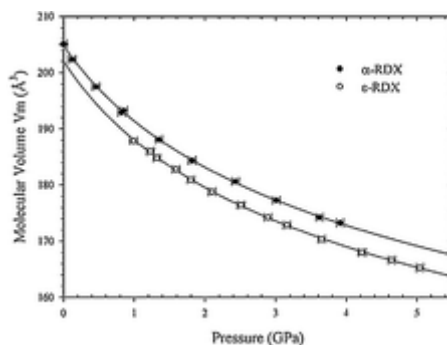
Although there is only a very small decrease in molecular volume across the  $\gamma \rightarrow \epsilon$  transition, comparison of the structures shows significant differences. In the  $\epsilon$ -form the RDX molecules adopt the AAA conformation shown in Figure 3b. This is highlighted by reference to the angle  $\delta$ , which is defined as the angle between the plane of the C-N-C ring atoms and the corresponding N-N bond. The  $\delta$ -values for  $\epsilon$ -RDX are presented in Table 1 alongside the corresponding values for both molecules in  $\gamma$ -RDX,  $\alpha$ -RDX, and for the isolated molecule in the AAA conformation as calculated using DFT methods.<sup>12</sup>

**Table 1.** Values of  $\delta$  (in  $^\circ$ ) for different conformations of RDX

$\epsilon$ -form	$\alpha$ -form	$\gamma$ -form (molecule 1)	$\gamma$ -form (molecule 2)	AAA <sup>a</sup>
35.5	33.4	39.6	39.6	30.3
36.3	33.9	17.3	17.3	30.1
42.7	-19.8	-2.4	9.5	29.9

<sup>a</sup> calculated from ref. 12

Furthermore, a major reorientation of at least one of the molecules must also occur in order to achieve the packing displayed in  $\epsilon$ -RDX. In the  $\gamma$ -form the two inequivalent molecules are arranged over a pseudo-inversion centre (a result of the  $\alpha \rightarrow \gamma$  transition), but the molecules in  $\epsilon$ -RDX ( $Z' = 1$ ) adopt a head-to-tail packing arrangement.



**Figure 4.** Variation of molecular volumes of  $\alpha$ - and  $\epsilon$ -RDX with pressure.

At 3.65 GPa the  $\epsilon$ -form is 2.2% more dense than the  $\alpha$ -form (at 3.62 GPa), and the  $\epsilon$ -form remains the denser form at all studied pressures (see Figure 4). Even the extrapolated density of the  $\epsilon$ -form at ambient pressure indicates that it has a higher density than  $\alpha$ -RDX under the same conditions. The smooth variation in volume upon decompression of the  $\epsilon$ -form from 5.04 GPa to 0.99 GPa can be fitted to a Murnaghan equation of state<sup>13</sup> with  $V_0 = 808.3(3.7) \text{ \AA}^3$ ,  $B_0 = 10.34(0.84) \text{ GPa}$ ,  $B' = 7.78(0.31)$ .

Both the current study and the study by Miller observe that the  $\epsilon$ -form can be recovered almost to ambient pressure (0.75 GPa) when decompressed at ambient temperature. Combined with Miller's observation that the transition is reversible at elevated temperatures, this strongly suggests that the  $\epsilon$ -form is thermodynamically unstable with respect to the  $\alpha$ -form at ambient conditions, but may persist because of a significant kinetic barrier arising from re-orientation of neighbouring molecules. If this interpretation is correct, it would seem reasonable that the  $\epsilon$ -form could be recovered to ambient pressure if decompression occurred at sub-ambient temperatures, and hence we set out to explore this possibility. Using a Paris-Edinburgh cell equipped with the variable temperature insert, a sample of  $\epsilon$ -RDX- $d_6$  was prepared in a similar manner as described above. On reducing the temperature to 150 K and decompressing the sample gradually to ambient pressure, the diffraction pattern of the  $\epsilon$ -form persisted. Diffraction patterns were then recorded at 10 K intervals and the  $\epsilon$ -form persisted to 230 K. Over a period of 2h at this temperature, the sample gradually transformed to give the  $\alpha$ -form. A diffraction pattern was recorded for the  $\alpha$ -form at 220 K in order to compare the difference in molecular volumes between the two forms at this temperature - the results show unequivocally that the  $\epsilon$ -form is 0.86% more dense than the  $\alpha$ -form (see Table 2). It also proved possible to determine an expression for the volumetric thermal expansion coefficient of the  $\epsilon$ -form over the temperature range 150-220 K  $\{\alpha_v = \partial (\ln V) / \partial T = [1.99(5) + 0.010(5) * (T - 185)] \times 10^{-4} \text{ K}^{-1}\}$ . By integrating this expression from 220 K to 293 K and using the  $\epsilon$ -form volume at 220 K, it is possible to obtain another estimate of the unit-cell volume at 293 K and zero pressure. This gives  $V_0 = 819.4(2.2) \text{ \AA}^3$ , which is slightly higher than, but in reasonable agreement with the value found from the Birch-Murnaghan equation of state.

**Table 2.** Representative unit cell parameters for the four polymorphs of RDX.<sup>a</sup>

	$\alpha$ -form	$\beta$ -form <sup>5</sup>	$\gamma$ -form <sup>6</sup>	$\varepsilon$ -form
Space Group	<i>Pbca</i>	<i>Pca2</i> <sub>1</sub>	<i>Pca2</i> <sub>1</sub>	<i>Pca2</i> <sub>1</sub>
<i>a</i> (Å)	13.1661(40)	15.0972(7)	12.5650(19)	7.5191(41)
<i>b</i> (Å)	11.5393(38)	7.4563(6)	9.4769(6)	11.6430(49)
<i>c</i> (Å)	10.6668(28)	14.3719(11)	10.9297(9)	9.1765(39)
<i>V</i> (Å <sup>3</sup> )	1620.6(5)	1621.0(2)	1301.5(2)	803.4(4)
<i>Z</i>	8	8	8	4
<i>T</i>	220	150	293	220

<sup>a</sup> Data for the  $\alpha$ - and  $\varepsilon$ -forms refer to RDX-*d*<sub>6</sub>, and data for the  $\gamma$ - and  $\delta$ -forms refer to RDX-*h*<sub>6</sub>; data were collected at 5.2 GPa for the  $\gamma$ -form.

In conclusion, the crystal structure of the high-temperature, high-pressure polymorph of RDX, now denoted the  $\varepsilon$ -form, has been determined. It is more dense than the  $\alpha$ -form at 3.6 GPa and this remains the case over a wide pressure range. On this basis, the detonation velocity of the  $\varepsilon$ -form should be greater<sup>1</sup> and this has implications for the modelling of the performance characteristics of RDX, especially as the pressure/temperature regime under which the  $\varepsilon$ -form is obtained is closer to the conditions typical of detonation. The  $\varepsilon$ -form can be recovered to ambient pressure at 150 K and persists on warming to 220 K before transforming to the less dense  $\alpha$ -form at 230 K. This result has significance for the search for new forms of new high-pressure forms of energetic materials that may potentially be recovered to ambient pressure. Such forms might have enhanced properties such as higher detonation velocities or reduced sensitivities. The work highlights the variable temperature capability recently developed for the Paris-Edinburgh cell, which has enabled us to access temperatures over the range 150-473 K with a very high degree of control.



## Notes and references

[‡] Crystalline samples of RDX (SME type II; 100–300  $\mu\text{m}$ ) were kindly provided by W.G. Proud (Cavendish Laboratory, University of Cambridge). RDX- $d_6$  for neutron diffraction studies was prepared by nitration of hexamine- $d_{12}$ .<sup>14</sup> High-pressure neutron powder diffraction data were collected using the PEARL/HiPr diffractometer at the UK spallation neutron source, ISIS, located at the STFC Rutherford Appleton Laboratory. X-ray experiments were performed on non-deuterated RDX using a Merrill-Bassett diamond-anvil cell<sup>15</sup> equipped with 600  $\mu\text{m}$  culets and a tungsten gasket with a 300  $\mu\text{m}$  hole. A 4:1 mixture of methanol-ethanol was used as a hydrostatic pressure medium with a ruby chip acting as pressure calibrant.<sup>16</sup> X-ray diffraction intensities were collected using Mo- $K\alpha$  radiation on a Bruker SMART APEX II CCD diffractometer.<sup>17</sup> Single crystal data were processed according to the procedure described by Dawson *et al.*<sup>18</sup> X-ray data:  $\epsilon$ -phase  $\text{C}_3\text{H}_6\text{N}_6\text{O}_6$   $M = 222.12$ , orthorhombic, space group  $Pca2_1$ ,  $a = 7.032(1)$ ,  $b = 10.530(3)$ ,  $c = 8.791(1)$   $\text{\AA}$ ,  $V = 651.0(2)$   $\text{\AA}^3$ ,  $T = 293$  K,  $P = 5.70(5)$  GPa,  $Z = 4$ ,  $\mu = 0.216$   $\text{mm}^{-1}$ ,  $D_c = 2.266$   $\text{Mg m}^{-3}$ ,  $\lambda = 0.71073$   $\text{\AA}$ ,  $\theta_{\text{max}} = 26.910^\circ$ , 3740 reflections measured, 333 unique ( $R_{\text{int}} = 0.0916$ ). Final residuals for 61 parameters were  $R_1 = 0.0578$ ,  $wR_2 = 0.1102$  for  $I > 2\sigma(I)$ , and  $R_1 = 0.0875$ ,  $wR_2 = 0.1308$  for all data. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x or CCDC reference number 769778.

- [1] J. Akhavan in "The Chemistry of Explosives", 2<sup>nd</sup> edn., Royal Society of Chemistry, Cambridge, UK, 2004.
- [2] P. Hakey, W. Ouellette, J. Zubietta and T. Korter, *Acta Crystallogr., Sect. E*, 2008, **E64**, o1428
- [3] C.S. Choi and E. Prince, *Acta Cryst.*, 1972, **B28**, 2857.
- [4] W.C. McCrone, *Anal. Chem.*, 1950, **22**, 954.
- [5] D.I.A. Millar, I.D.H. Oswald, D.J. Francis, W.G. Marshall, C.R. Pulham, A.S. Cumming, *Chem. Commun.*, 2009, **5**, 562.
- [6] A.J. Davidson, I.D.H. Oswald, D.J. Francis, A.R. Lennie, W.G. Marshall, D.I.A. Millar, C.R. Pulham, J.E. Warren and A.S. Cumming, *CrystEngComm*, 2008, **10**, 162
- [7] J.A. Ciezak, T.A. Jenkins, Z. Liu and R.J. Hemley, *J. Phys. Chem. A*, 2007, **111**, 59
- [8] J. A. Ciezak and T. A. Jenkins, *Propellants. Explos. Pyrotech.*, 2008, **33**, 390
- [9] B.J. Baer, J. Oxley and M. Nicol, *High Pressure Res.*, 1990, **2**, 99
- [10] P.J. Miller, S. Block, G.J. Piermarini, *Combust. Flame*, 1991, **83**, 174

- [11] W.G. Marshall, D. J. Francis, C. J. Barry, M. G. Tucker, C. R. Pulham, G. Kouzmenko, and O. Kirichek, *manuscript in preparation*.
- [12] T. Vladimiroff and B. M. Rice, *J. Phys. Chem. A*, 2002, **106**, 10437
- [13] F.D. Murnaghan, *Proc. Nat. Acad. Sci.*, 1944, **30**, 244.
- [14] S. Bulusu, J. Autera and T. Axenrod, *J. Labelled Compd. Radiopharm.*, 1980, **17**, 707
- [15] L. Merrill and W.A. Bassett, *Rev. Sci. Instrum.*, 1974, **45**, 290
- [16] G.J. Piermarini, S. Block, J.D. Barnett and R.A. Forman, *J. Appl. Phys.*, 1975, **46**, 2774
- [17] Bruker-Nonius, APEX-II, Bruker-AXS, Madison, WI, USA, 2000.
- [18] A. Dawson, D.R. Allan, S. Parsons and M. Ruf, *J. Appl. Crystallogr.*, 2004, **14**, 433.